Absorption of toluene by vegetable oil–water emulsion in scrubbing tower: Experiments and modeling

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HIGHLIGHTS

- Absorption of toluene per a vegetable oil water emulsion.
- Vegetable oils used as organic solvent for VOCs absorption.
- Experimental Henry constants values for toluene with sunflower oil.
- Oil cover ratio to appreciate the real interfacial area offer by the droplet emulsion.
- Special modeling approach for mass transfer by an emulsion.
- A transfer model has been established for an emulsion.
- A thermal regeneration (120 °C) of the oil water emulsion.

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ABSTRACT

The aim of this work is to study continuous counter current absorption of Volatile Organic Compounds (VOCs) by an oil water emulsion. This process enables the treatment of hydrophilic and hydrophobic VOC within a gaseous effluent emitted by chemical or food processing industries. Toluene was chosen as the pollutant in this work because of its hydrophobicity and its widespread use in chemical industries. As organic solvents for VOC absorption, vegetable oils were proposed for the treatment process to reduce the impact on the environment. The absorbing oil was selected for its good absorption capacities, its chemical and thermal stability and its low cost. To test their impact on the operational efficiency of the absorption process, numerous parameters were varied, such as liquid and gas flow rates, temperature and nozzle type. Thermal regeneration (120 °C) of the oil was proposed and tested on the experimental device. No impact on efficiency was noted, even after several regenerations. Finally a model was de termined to predict the effects of operational conditions on the absorption efficiency of an emulsion.

1. Introduction

Volatile Organic Compounds (VOCs) are molecules composed mainly of carbon, hydrogen and other atoms like oxygen, nitrogen, sulfur or halogens. They have a high vapor pressure, usually greater than 10 Pa (Council directive 1999/13/EC, 1999). This property results in a low boiling point, which causes large num bers of these molecules to evaporate and to be release into the atmosphere. VOCs are present in the gas released in numerous industries, such as food/agriculture, electronics, wastewater treatment, painting/coating manufacture, petrochemical pro cesses, and highway construction, and generate pollution and unpleasant odors. Released into the tropospheric atmosphere, VOCs can react with NOx in presence of solar radiation to form ozone, which is a very strong pollutant molecule. Its influence on human health can be critical, especially in the chemical industry, where long exposure could promote the development of cancers. VOCs can be foul smelling, oncogenic, teratogenic or mutagenic (Hueper et al., 1962; Somers, 2011; Sram et al., 2007). In addition to irritation of the mucous membranes, skin and eyes, other risks affecting the central nervous system are commonly associated with VOCs. As a consequence of those risks, limit values have been set by the World Health Organization, restricting the concentra tions to which people can be exposed and, in late 2013, the

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International Agency for Research on Cancer assessed the carcinogenicity of outdoor air pollution (Loomis et al., 2013). Consequently, rules concerning industrial gas emissions are gradually becoming stricter. Processes could be optimized and the use of solvents reduced in order to decrease the VOC concentration in the air but, unfortunately these actions are not sufficient or cannot be applied in all chemical processes. Thus specific treatments have to be used to reduce emissions, with the aim of eliminating or recovering VOCs. Eliminative treatments, such as thermal processes and biochemical methods, have been developed recently but many of them are still in the research or development phases with new and innovating technologies (Khan and Ghoshal, 2000). Recovery could be achieved by several methods: condensation, absorption, adsorption and membrane separation. The most commonly used is adsorption, classically with activated carbon (Subrenat and Le Cloirec, 2006). It is usually a batch process, using heating or stripping with steam for the regeneration, and is limited by the adsorbent capacities (Hester and Harrison, 1995). Absorption is based on the transfer of the soluble gas molecule to a solvent liquid (water or low volatility hydrocarbon molecules). An absorption tower can be used for high VOC concentrations (500 5000 ppm). A condensation technique can also treat waste gases with high VOC concentrations but it is more suitable for organic pollutants with high boiling points. Absorption is used to remove VOCs from the gaseous effluent by creating a contact between the liquid solvent and the contaminated gas. Soluble VOCs can transfer to the liquid and the air stream is scrubbed. This operation takes place in a tower designed to provide the contact area necessary to perform the mass transfer. Trays and packed columns or atomizers can provide such contact (Roustan, 2003). Scrubbing promotes gas liquid contact by using packing material, which can either be randomly dumped or stacked in the tower. It varies widely in shape, size, cost, contact surface area, pressure and material of construction and each packing design has its own advantages (Kherbeche et al., 2013). The packing increases the contact surface area between the phases and reduces the height needed for the tower (Bhatia et al., 2004) but the pressure drop and energy needed are much greater than in empty spray towers (Brasquet and Le Cloirec, 1997). Packed towers are also more expensive and more sensitive to clogging, especially for flue gas treatment, and they cannot be adapted for viscous solvents such as oil. As the VOCs can be hydrophilic or hydrophobic, water is widely used as an absorbent of hydrophilic VOCs (Biard and Couvert, 2013) and oil is used for hydrophobic VOCs. However, two columns are necessary and the high viscosity of oil makes the energy expenditure prohibitive for this application (Darracq et al., 2010). The use of a water/oil emulsion is an alternative that reduces the number of towers of a process (Tatin et al., 2015) and thus reduces the initial investment in equipment and the cost of energy supplies while increasing the contact surface area available for gas liquid exchange and the amount of VOCs that can be treated in a counter current packed system (Dumont et al., 2011). So, when the goal of the treatment is to absorb both hydrophilic and hydrophobic VOCs by using an emulsion, the spray column is the most appropriate apparatus to handle the viscosity issue. Other works have been published on the absorption method using a siloxane/water emulsion (Dumont et al., 2012), or silicone oil/water emulsion (Tatin et al., 2015). Most of these studies operated in a semi batch system using recirculation of the emulsion without any regeneration of the VOC saturated oil. To date, no work has dealt with the regeneration of the solvent, which is nevertheless a major step of the global process if steady state operation is desired. Obviously, regeneration has the advantages of (i) reducing the solvent consumption and (ii) enabling the VOC to be recovered when this constitutes added value for the process. The originality of the present study basically lies in the selection of the absorbent oils. The vegetable oils chosen were environmentally friendly, without any oil VOC release and had good temperature resistance. Thus thermal regeneration of the oil was possible to ensure continuous treatment of the polluted gas with lower oil consumption. The first objective of this paper is to characterize the absorption process in the aim of evaluating the influence of temperature, nozzle size, gas and liquid flow rates, and regeneration on the process efficiency. The second objective is to establish a model to describe the continuous absorption processes at steady state in function of flow rates and temperature.

2. Material and methods

2.1. Vegetable oil characteristics

The use of vegetable oils as organic solvents for VOC absorption has been proposed to reduce the impact on the environment. Vegetable oils have shown good affinity for the capture of VOCs such as toluene. Two kinds of sunflower oils were selected: a commercial (30.2% Oleic Acid) and high oleic sunflower oil (HOSO, with 86.3% Oleic Acid) obtained from sunflower seeds purchased by Arterris (*France*). Before choosing an oil for the absorption process, it is recommended to study its physical properties in order to predict its behavior under the experimental conditions. The physicochemical characteristics of the sunflower oils measured and studied in this work are reported in Table 1.

Oil oxidation reactions leading to oil degradation with loss of properties, could occur during the VOCs absorption experiments. The oxidative stability of oil depends on the fatty acid composition of its constituent triacylglycerol. The inherent stability is a theoretical value defined as the weighed sum of relative oxidation rates multiplied, respectively, by the percentage content of each constituent fatty acid, in such a way that the lower the inherent stability value, the more stable an oil is. The inherent stability of HOSO was 1.9 versus 6.8 for commercial sunflower oil (Erickson, 2006). Highly unsaturated such as oil rich in linoleic acid are especially susceptible to the autoxidation reactions and the Iodine value is a measure of the average number of double bond of an oil. For comparison, the oxidation rate of linoleic acid is 10 times the oxidation rate of oleic acid. HOSO was chosen in this work in because it presented a lower iodine value, correlated to the content in monounsaturated and polyunsaturated fatty acids (Table 1), than commercial sunflower oil. Indeed lower is the iodine value, better is the inherent stability of the oil and higher was the ability of the oil to keep its properties (Erickson, 2006; Dufaure et al.,

Table 1
Physicochemical characteristics of the sunflower oils studied.

Candidate oils	Density (kg/m^3)	Viscosity (Pa s)	Surface tension (mN/m)	Iodine Value (cg I_2/g)	Saturated fatty acids (%)	Monounsaturated fatty acid (oleic acid)	Polyunsaturated fatty acids (linoleic acid)
HOSO	910.91 ± 0.1	0.077 ± 0.001	34.32 ± 1	85 ± 0.1	6.5	89.5% (86.3%)	3.9% (3.8%)
Commercial sunflower oil	918.25 ± 0.1	0.057 ± 0.001	34.89 ± 1	125 ± 0.1	10.8	30.5% (30.2%)	58.7% (58.7%)

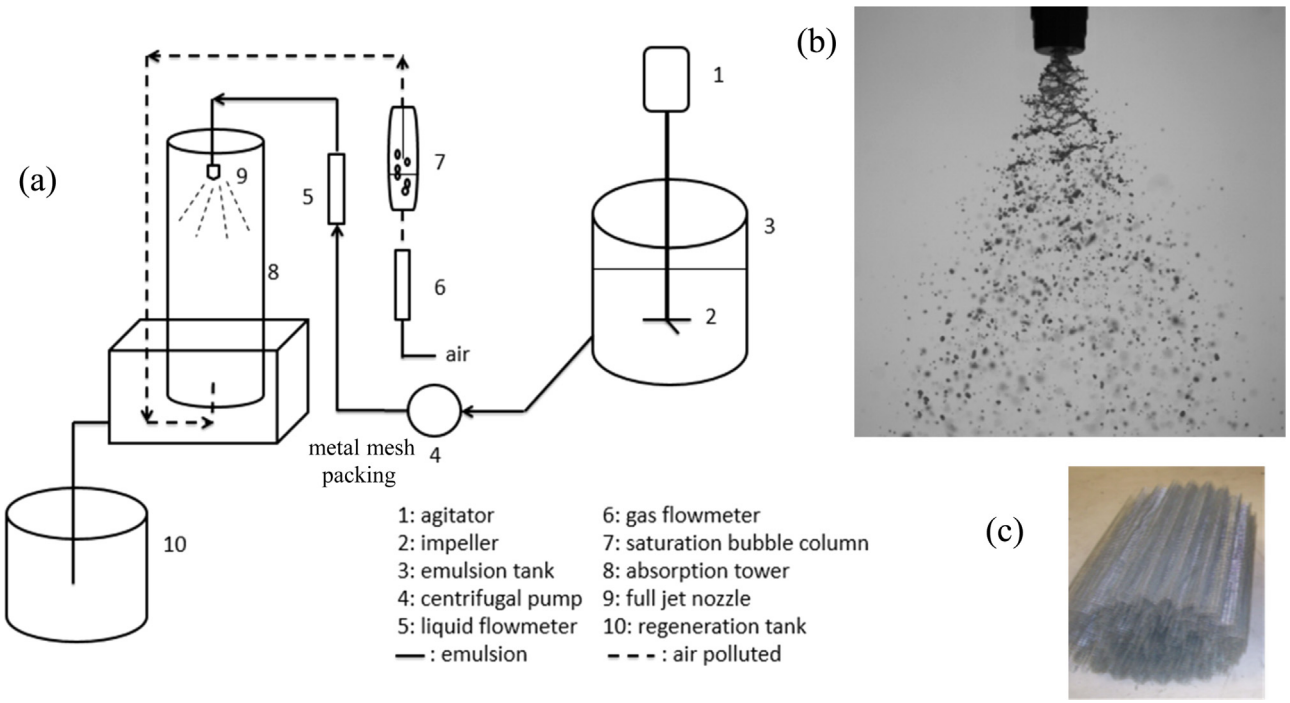

Fig. 1. (a) Experimental setup (b) high speed camera visualization of the emulsion spray (c) packing used.

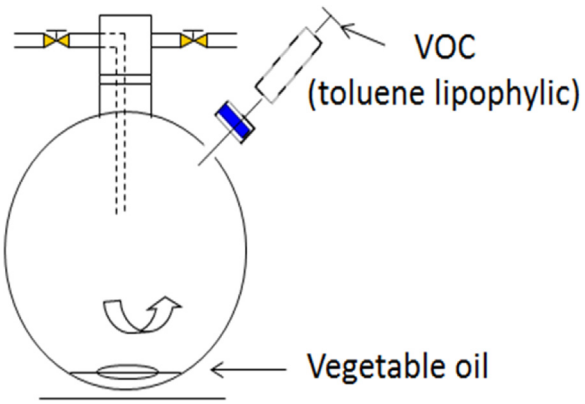

Fig. 2. Experimental setup for determination of Henry's constant.

1999, 2000). As sunflower oil is more viscous than water, it could be difficult to transport oil from the tank to the full jet nozzle. Then water can be a good liquid vector to resolve this issue. Moreover, oil surface tensions are lower than the surface tension of tap water (70 mN/m), inducing a spray of smaller droplets when emulsion is considered, and thus leading to a favorable oil inter facial area.

2.2. Spraying column

The experimental setup used was a transparent PMMA polymer (Poly Methyl MethAcrylate) column 0.2 m in diameter and 0.7 m in height (Fig. 1). The pump sprayed emulsion through a full jet nozzle (Spraying System&Co, USA) placed at the top of the column. Three sizes of nozzle were tested during the experiments, having internal diameters of 0.64, 1 and 1.3 mm. The emulsion was pre pared in advance in a tray (3) for 2 h. No surfactant was added to stabilize the emulsion but we observed a certain stability due to double effect of the mixing performed in the storage tank and the spraying. An air flow polluted with a controlled amount of toluene was introduced at counter current at the bottom to simulate pollution. This polluted air flow was obtained at atmospheric temperature and pressure by bubbling air into a saturation bubble column containing liquid toluene (7). The liquid emulsion and polluted air flowed at countercurrent in the column in an open circuit. A photoionization detector (PID) system (RAE3000) was used to measure the input and output concentrations of toluene in the column and so to track the evolution of the VOC absorption efficiency versus time. The RAE3000 is a PID that has an extended detection range from 0 to 15,000 ppm, a rapid three second re sponse time, and built in correction factors for more than 200 compounds, so it can measure chemicals fast and accurately. A homemade packing with a high voidage was also tested during the experiments to simulate a packed tower scrubber. The character istics of this packing have been defined by Moustiri et al. (2002).

2.3. Henry's law constant determination

The Henry's law constants of the toluene with oils under test were determined by an equilibrium method. A glass ball with a volume of 2 l (Fig. 2) was used to perform the Henry's law constant determination. A small amount of toluene (0.2 ml) was injected into the glass ball by a syringe via a septum. After its complete vaporization, the VOC concentration was measured by the RAE3000 PID system. Then, 5 ml of sunflower oil in water was injected by a syringe into the ball via the septum. Mixing was ensured by an electrostatic mixer, and a 60 min delay was allowed to reach the equilibrium state. It is generally sufficient to wait 40 min to reach the steady state concentration but we made sure that the equilibrium condition had been attained by waiting longer. A new VOC concentration measurement was performed after this step. Eq. (1), coming from a mass balance, was then used to recalculate the Henry's law constants for toluene and the oils under test.

$$m = \frac{\left([VOC]_{equi} . \frac{V_{Mair}}{V_{air}} \right)}{\left(\left([VOC]_{before\ \ equi} - [VOC]_{equi} \right) . \frac{V_{Mliquid}}{V_{liquid}} \right)} \quad (1)$$

where

$$m = \frac{H}{P} \tag{2}$$

The oil with the smallest Henry's law constant was the best oil to use for the toluene absorption.

2.4. Oil regeneration

It is very important to evaluate the possibility of regenerating oils thermally. Their regenerative capacities control the viability of the absorption process and the possible reuse of VOCs. The oil polluted by toluene was separated from the oil in water emulsion (5% v/v) by gravity decantation. Then the oil polluted by toluene was heated at 120 °C in a 2.5 L double jacketed open reactor for 2 hours under dry nitrogen flow and 200 rpm mechanical stirring. The toluene content in the regenerated oil was measured by PID and the oil could be re used for a new air purification experiment. A sufficient volume of oil was produced by the regenerative method and then used as a solvent in our pilot to validate the viability at a larger scale.

2.5. Interfacial area

A high speed camera (APX Photron, 4000 images/s), the image processing toolbox of MATLAB and a LitePad HO LED light panel (Rosco®) were used to measure the size distributions and velo cities of the droplets during the experiments and to estimate the corresponding interfacial area by Eq. (3). Fig. 1c shows an example of the images used for the treatment.

$$a^0 = \frac{6.\,L'}{d_D{\cdot}\Omega{\cdot}U_{effective}} \tag{3}$$

where L′ is the volume liquid flow, d_D is the average droplet dia meter estimated from Eq. (12), $U_{effective}$ is the measured droplet velocity and Ω is the column cross section. Because toluene is not absorbed in water (Tatin et al., 2015), we had to consider only the oil interfacial area involved in the mass transfer operation. We introduced an oil cover ratio (α), which is directly linked to the oil: water emulsion ratio if we assume an isotropic emulsion. This assumption has been experimentally verified by Tatin (2008) for an emulsion at 5% and 10% oil by volume. So, for an emulsion at 5% oil by volume, a cover ratio (α) of 0.05 means that only 5% of the surface of an emulsion droplet is occupied by oil.

2.6. Efficiency

At the start, only the gaseous effluent was sent into the bottom of the column. Some time was needed to reach the steady flow condition where inlet and outlet concentrations were equal. The concentration of toluene was measured continuously through the RAE PID system. When the concentration in the column was homogeneous, the emulsion could be sprayed. Then a certain time was required to reach a stable value of y_{out}. Knowing the inlet and the outlet concentrations of VOC in the column, the efficiency could be estimated using the following equation:

$$E_G = \frac{y_{in} - y_{out}}{y_{in}} \tag{4}$$

where:

y_{in}: is the mole fraction of toluene within the gas phase (air) at the bottom of the column.
y_{out}: is the mole fraction of toluene at the top of the column.

3. Modeling

The proposed model provides a way to estimate the efficiency of the absorption column for different operating conditions under test. The model is described for a single VOC (toluene), for a single absorbent phase (vegetable oil under test), operating at counter current of gas and liquid. In that case, the height of the column to reach the desired efficiency is given by the following equation:

$$Z = HTU_{0G}{\cdot}NTU_{0G} = \frac{G}{K_G^0.\,a^0.\,\alpha.\,\Omega}\left[\frac{A^*}{A^* - 1}.\,\ln\left(\frac{A^* - E_G}{A^*.\,(1 - E_G)}\right)\right] \tag{5}$$

where:

HTU_{0G} is the height transfer unit in the gas phase; it is related to the gas flow rate, the interfacial area, the global transfer re sistance K_G^0 and the cross section of the column; α is the cover ratio defined in the Material and Methods section; it represents approximately the oil area offered by the droplets to the mass transfer operation. The efficiency E_G can be deduced from Eq. (5) if all the other parameters can be estimated.

NTU_{0G} is the number transfer unit and it depends on A^*, the absorption rate defined by.

$A^* = \frac{L}{m.G}$ with L and G the molar liquid flow and the molar gas flow, respectively.

Many models are proposed in the literature to characterize mass transfer. We choose, here, the model that considers the presence of transfer resistance within both phases (gas and liquid). The double film model defines the global transfer resistance K_G^0 as the sum of two resistances, one from the liquid side, k_L^0, and the other from the gas side, k_G^0.

3.1. Determination of K_G^0

Knowing the local mass transfer coefficients, k_L^0, k_G^0 and (m) we calculate K_G^0 from:

$$\frac{1}{K_G^0} = \frac{1}{k_G^0} + \frac{m}{k_L^0} \tag{6}$$

The mass transfer coefficients k_G^0 and k_L^0 are determined from Frossling's (1938) and Saboni's (1991) correlations respectively.

3.2. Determination of k_G^0

The Frössling correlation (Frössling, 1938) is used to predict the value of k_G^0, which can be estimated from k_G:

$$Sh_G = 2 + 0.60\ Re_D^{0.05}\ Sc_G^{0.33} \tag{7}$$

where:

Sh_G, the Sherwood number, $= \frac{k_G{\cdot}\,d_D}{D_{toluene-air,G}}$;

Sc_G, the Schmidt number, $= \frac{\mu_G}{\rho_G{\cdot}D_{toluene-air,G}}$;

and Re_D, the Reynolds number, $= \frac{U_D{\cdot}d_D{\cdot}\rho_G}{\mu_G}$.

3.3. Determination of k_L^0

The liquid phase mass transfer coefficient k_L^0 can be estimated from k_L using a correlation proposed by Saboni (1991):

$$Sh_L = 0.8{\cdot}Re_i^{0.5}{\cdot}Sc_L^{0.5} \tag{8}$$

where

Sh_L, the Sherwood number, $= \frac{k_L{\cdot}d_D}{D_{toluene-oil,L}}$;

Sc_L, the Schmidt number, $= \frac{\mu_{water}}{\rho_{water}{\cdot}D_{toluene-oil,L}}$;

and Re_i, the Reynolds number, $= \frac{U^* \cdot d_D \cdot \rho_{water}}{\mu_{water}}$;

The surface friction velocity U^* was calculated through the surface shear stress τ_s:

$$U^* = \sqrt{\frac{\tau_s}{\rho_L}} \tag{9}$$

$$\tau_s = \frac{1}{2}. \rho_G. U_D^2. C_D \tag{10}$$

where C_D is the drag coefficient for a solid sphere, calculated by the following relation

$$C_D = \frac{24}{Re_D}\left(1 + 0.15 \cdot Re_D^{0.687} + \frac{0.0175}{1 + 4.25.10^4 \cdot Re_D^{-1.16}}\right) \tag{11}$$

3.4. Droplet sizes

Droplet size is a very sensitive parameter in the model. Murty's correlation (Roustan, 2003) was used and modified to match our experimental droplet size. Experimental measurements of the droplet size showed a decrease in the size according to the liquid flow rate for a given gas flow rate. The diameter ranged from 1.2 ± 0.05 mm to 0.6 ± 0.05 mm for liquid flowrates from 0.5 to 1.15 L/min. The following correlation was established to estimate the droplet sizes:

$$d_D = 57 \cdot Re^{-0.48} \cdot We^{-0.18} \cdot D_{\text{nozzle}} \tag{12}$$

where:

$Re = \frac{U_{nozzle} \cdot D_{nozzle} \cdot \rho_{water}}{\mu_{water}}$.

We, the Weber number $= \frac{U_{nozzle} \cdot \mu_{water}}{\sigma_{water}}$.

This droplet size will be used to calculate a^0.

3.5. Efficiency prediction

Once all the unknown parameters have been determined, we can now calculate the theoretical efficiency E_G as follows:

$$E_G = \frac{A^* - A^* e^{\frac{NTU_{0G}(A^*-1)}{A^*}}}{1 - A^* e^{\frac{NTU_{0G}(A^*-1)}{A^*}}} \tag{13}$$

where NTU_{OG} is calculated as:

$$NUT_{OG} = \frac{Z}{HUT_{OG}} \tag{14}$$

4. Results

4.1. Henry's law constant

In order to select the best oil for the absorption process, an evaluation of the Henry constant was performed. This parameter represents the capacity of the oil to absorb gaseous toluene. For both oils, the measurement was performed three times at ambient temperature. The Henry's law constant was averaged over the three measurements. The results are shown in Table 2.

Firstly, good reproducibility is observed (standard deviation less than 5%) for each oil. Secondly, the m value is larger than for silicone oil/toluene (Tatin et al. (2015), $m = 0.012$). Finally, it can be observed that the Henry's law constant for the HOSO (87% oleic acid) is 20% smaller than that of the commercial sunflower oil and it would potentially be preferable as a solvent in an absorption column.

4.2. Efficiency versus liquid flow for different oil types

The efficiency E_G is shown as a function of liquid flow rate, ranging from 0.8 to 1.3 L/min, in Fig. 3 for a 5% (v/v) emulsion in water for the two oils and air polluted with toluene. According to Fig. 3, regardless of the value of the gas flow rate, the efficiency of the HOSO (♦ symbols) and the commercial sunflower oil (■ symbols) is similar (less than 3% difference). The values did not differ significantly from a statistical point of view whether HOSO or the commercial sunflower oil was used, whereas the Henry's law constants were different. This could be explained by the physico chemical properties of the oils. The surface tensions are similar but viscosities are different. A higher viscosity, for the HOSO, will lead to larger droplets (Dietrich et al., 2012), which is disadvantageous for the mass transfer area but could improve the liquid side mass transfer coefficient. Finally, since efficiency is the almost the same, HOSO, which presented better absorption performance and suitable chemical stability was selected for the end of the study.

4.3. Efficiency versus operating parameters (HOSO)

The efficiency, E_G, of the process is now evaluated for several parameters: liquid flow rate, gas flow rate, and packing and nozzle diameter. Each experiment consisted of varying one parameter and maintaining the others constant in order to evaluate the impact of the parameter in question on the efficiency of absorption. The following parameters were selected as a basis: liquid flow rate: 1 L/min, gas flow rate: 14 L/min, full cone nozzle (diameter 1.3 mm), and emulsion composition: 5% oil v/v and 95% water v/v, HOSO (87% oleic acid), and no packing within the column.

4.3.1. Liquid flow

To evaluate the impact of liquid flow rate on efficiency, three liquid flow rates were used: 0.8; 1 and 1.15 L/min; all other parameters given previously remained fixed. The results are shown in Fig. 3 (♦ symbols). It appears that the increase in liquid flow rate led to an increase in efficiency. A reduction of about 40% in the liquid flow rate induced a decrease of about 10% in the efficiency. An increase in liquid flow rate induced a larger interfacial area and a smaller residence time within the column, which had contradictory effects, but it was proved that the increase in interfacial area dominated. According to the theory, a decrease of the liquid

Table 2
Henry's law constant values obtained for toluene dissolving in the different vegetable oils used.

Oil	Commercial sunflower oil			HOSO			HOSO after regeneration		
Experiment	1	2	3	1	2	3	1	2	3
Temperature (°C)	24	23	20.8	24	23.7	23.2	22.6	23.1	25
Initial composition y_i (ppm)	3712	4440	4587	4783	4405	4367	4420	4426	5263
Equilibrium composition y_e (ppm)	665	888	892	932	805	836	815	830	944
m	0.0158	0.018	0.017	0.0152	0.014	0.0148	0.014	0.0144	0.0137
Average value of m	0.017			0.0147			0.014		

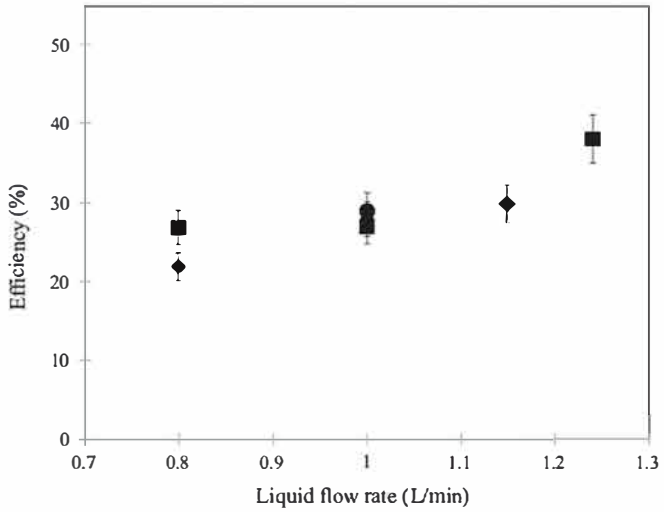

Fig. 3. Evolution of efficiency in function of the liquid flow rate ■ commercial sunflower oil ♦ HOSO (oleic acid 87%) • HOSO (oleic acid 87%) after 2 regenerations/absorption.

flow rate has a negative effect on absorption efficiency and on the absorption factor A^*, which was confirmed by these experiments.

4.3.2. Nozzle size

The nozzle size was also evaluated. Three different experiments were done with the same operating parameters, except for the diameter of nozzles, which had values of 0.64, 1 and 1.3 mm. The experimental results are reported in Fig. 4. The results show an efficiency of 23 ± 3% for all experiments. This does not mean that operating conditions and mass transfer had the same effects; it can be explained by opposing dual phenomena: the nozzle diameter controlled the droplet sizes: a droplet size decrease was observed when the nozzle diameter decreased, as established by Saboni (1991). This led to a larger interfacial area favoring the mass transfer. But, as droplets were smaller, velocities were also smaller, involving a decrease in the Reynolds number and mass transfer. Finally the two effects seemed to compensate each other and efficiency was constant.

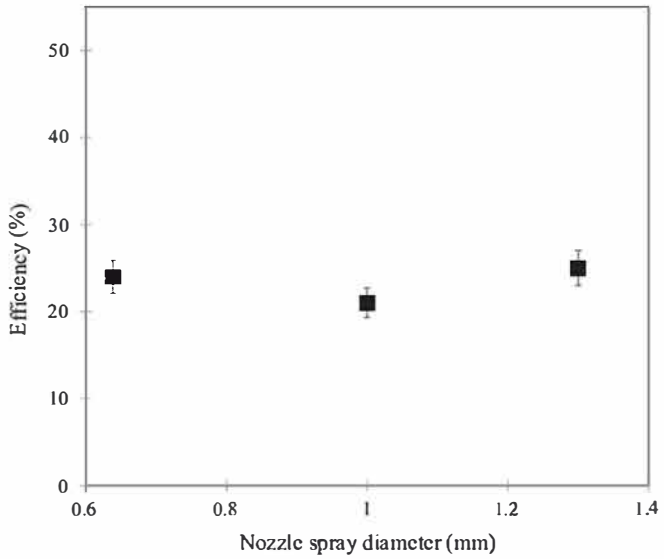

Fig. 4. Evolution of the efficiency in function of the nozzle spray diameter (HOSO – oleic acid 87%).

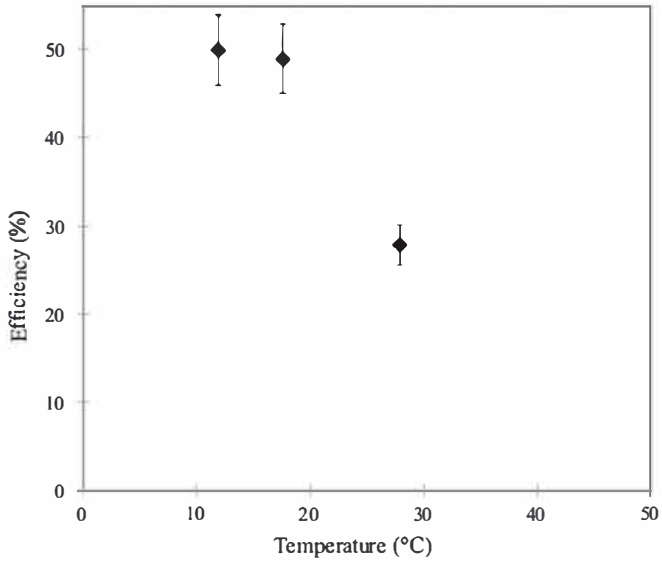

Fig. 5. Evolution efficiency in function of the temperature (HOSO – oleic acid 87%).

4.3.3. Temperature

Temperature is a very important parameter in absorption processes because of its strong influence on the Henry's law constant. This is due to the fact that gas liquid thermodynamic equilibrium is strongly dependent on temperature. Three temperatures were tested: 12 °C, 17 °C and 28 °C. The results of the efficiency for these temperatures are plotted in Fig. 5.

Experimental results showed that efficiency was higher when temperature decreased; confirming that Henry's law constant followed the Arrhenius law:

$$H = A.\exp\left(-\frac{B}{R.T}\right) \tag{15}$$

with:

A, B: experimental constants.
R: ideal gas constant (J mol $^{-1}$ K $^{-1}$).
T: absolute temperature (K).

4.3.4. Packing

The influence of the presence of a packed system was also investigated. The efficiency was measured, for the fixed operating conditions, with an empty tower and a packed tower as shown in Fig. 1c. The results are summarized in Table 3.

As noted in the table, efficiency was clearly improved by the presence of the special high porosity packing used. The packing split droplets into smaller ones, increasing the exchange area; global residence time increased, promoting the global mass transfer. No major increase in pressure drop was observed with this special packing.

4.3.5. Gas flow

Three gas flow rates (14, 18 and 23 L/min) were tested with the HOSO as solvent to investigate the influence of gas flow rate on efficiency. The different values of efficiency obtained for the different gas flow rates are presented in Fig. 6. As shown on the

Table 3
Efficiency versus packed/empty tower.

Tower type	Efficiency (%)
Empty tower	28
Packed tower	38

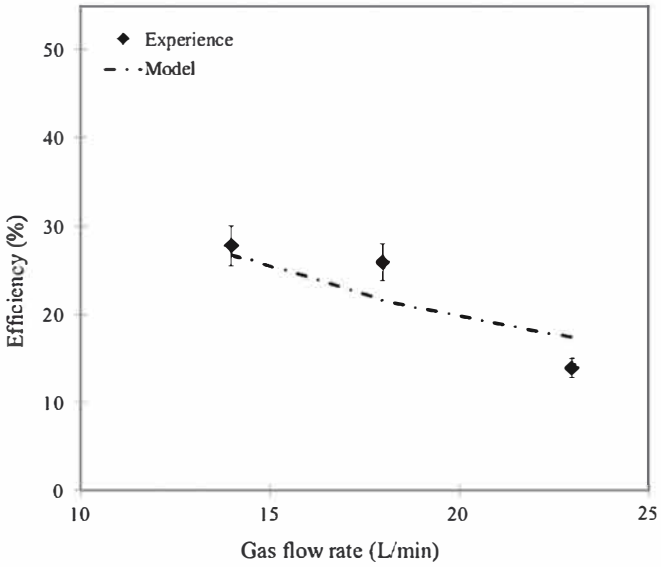

Fig. 6. Experimental and theoretical efficiency versus the gas flow rate (HOSO – oleic acid 87%).

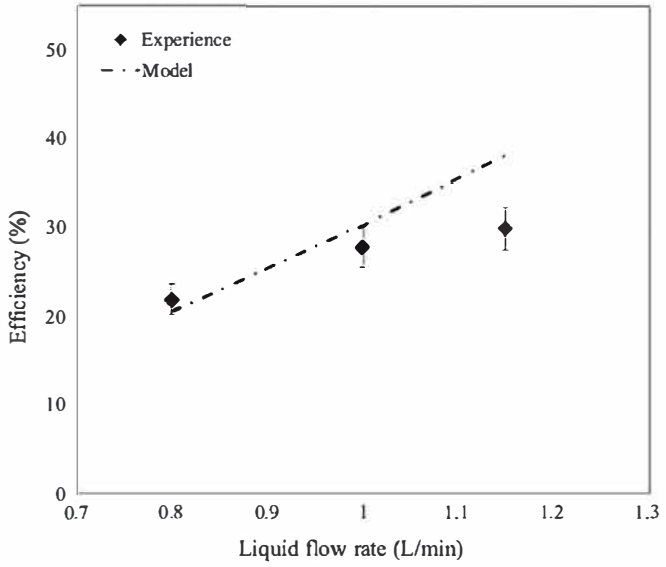

Fig. 7. Experimental and theoretical efficiency versus the liquid flow rate (HOSO – oleic acid 87%).

figure, efficiency increased when gas flow rate decreased. This was due to the absorption factor, which is inversely proportional to gas flow.

4.3.6. Oil regeneration

Finally, the impact of oil regeneration was studied. After the oil had been used for the absorption of toluene in the column, it was thermally regenerated in order to eliminate absorbed toluene. Then the whole process was repeated. After these two uses/re generations, the Henry's law constant of the oil and the process efficiency were measured.

The value of the Henry's law constant for regenerated oil is reported in Table 2. The value is almost the same as for the fresh oil. This means that, after two regenerations, the oil maintained the same quality and absorption capacity. The efficiency obtained with the regenerated oil for the classical operating conditions is reported in Table 4.

Experimental results showed that the absorption efficiency was the same before and after regeneration (as displayed efficiencies were determined at $\pm 3\%$). We thus conclude that regeneration did not affect the quality of the oil and this oil could be used several times.

4.4. Model results

The model results (Eq. (13)) are represented in Figs. 6 and 7 and illustrate a decrease in efficiency with an increase in gas flow, and an increase in efficiency for an increase in liquid flow, which is in satisfactory agreement with experiments. However, as gas flow or liquid flow increases, the accuracy of the model decreases. Nevertheless, the model gives good predictions of the absorption efficiency. A hydrodynamic study and the fundamental approaches of mass transfer were the basis on which this model was built. Variations of absorption efficiency can be well predicted by the model when gas or liquid flows are modified.

Table 4
Efficiency before and after regeneration.

HOSO	Efficiency (%)
Fresh oil	28
Oil after regeneration	29

5. Conclusion

This paper presents the absorption process of toluene using an oil/water emulsion at 5% by volume (v/v). The choice of the oil focused on vegetable (sunflower) oil to reduce the impact on the environment. These oils are very good candidates for VOC ab sorption, as they resist high temperatures, making thermal re generation possible; they do not emit VOC, and they are cheap. Henry's law constants for toluene were determined for different sunflower oils and the absorption process efficiency was evaluated for several parameters. The experimental results show that vege table oils with a high monounsaturated fatty acids content, such as HOSO (86.3% oleic acid), have a good absorption capacity with respect to toluene. These vegetable oils have a high molecular weight, which gives them some stability as solvents and a specific affinity with toluene. Numerous parameters were varied to test their impact on the operational efficiency of the absorption pro cess such as: liquid flow rate, temperature, and nozzle type. It was observed that efficiency decreased with the gas flow rate and temperature, increased with liquid flow rate and was not affected by the nozzle size in the range used in our study. For the condi tions under test, the toluene absorption efficiencies varied from 20% to 50%. A conventional model was presented in this study. It combined double film model theory, the concept of number of transfer units, and experimental results related to the thermo dynamics of the absorbent/fluid. This model was adapted to the case of a sprayed emulsion by an oil droplet cover ratio alpha, which was used to define the effective oil surface in contact with the gas to be treated. Both gas and liquid flow rates were varied to test the model and compare the calculated efficiencies with the measured ones. The experimental efficiencies were pretty well predicted by the model whatever the operating conditions under test, and the efficiency variations were well related. However, some predicted values could display a discrepancy of 20% with respect to experimental ones. The first cause of this significant error could be the oil cover ratio, which was taken to be equal to the emulsion ratio here. More experiments need to be performed now to identify an accurate relationship between oil:water ratio and surface area available for the transfer. The second reason could be related to a monodisperse droplet assumption; under real op erating conditions a droplet distribution exists. So, the model works for studying the absorption of toluene by sunflower oil

emulsion in the ranges of operating conditions tested in this study. The results show that the absorption of VOC by an oil water emulsion can be modeled using conventional approaches of che mical engineering. The driving force to be considered is oil and the interfacial area is the oil droplet interfacial area, water is only a vector for the oil. This model is now a suitable tool for predicting efficiency within an error of 6%. It can be improved to predict ef ficiencies as a function of temperature or nozzle diameter, in order to design industrial absorption systems involving emulsions. Fur ther investigations are planned to confirm the regeneration cap ability of HOSO oil by a greater number of regeneration steps.

6. Nomenclature

A^*	absorption rate [dimensionless]
a^0	effective superficial area [m^2 m^{-3}]
C_D	drag coefficient [dimensionless]
$D_{A,G}$	diffusion coefficient of a solute A in gas phase [m^2 s^{-1}]
D_{Nozzle}	nozzle inner diameter [m]
d_D	drop diameter [m]
E_G	efficiency of the spray tower [dimensionless]
G	molar gas flow [mol s^{-1}]
He	Henry's law constant [Pa]
HTU_{0G}	height of transfer unit in gas fluid [m]
K_G^0	global Material Transfer coefficient [mol m^2 s^{-1}]
k_G^0	mass transfer coefficient at gas film [mol m^2 s^{-1}]
k_G	mass transfer coefficient at gas film [m s^{-1}]
k_L^0	mass transfer coefficient at liquid film [mol m^2 s^{-1}]
k_L	mass transfer coefficient at liquid film [m s^{-1}]
L	molar liquid flow [mol s^{-1}]
L'	volumetric liquid flow [m^3 s^{-1}]
m	Henry's law constant in dimensionless form [dimensionless]
NTU_{0G}	number of transfer units in gas fluid [dimensionless]
P	total pressure [Pa]
R	ideal gas constant=8.314 [J mol^{-1} K^{-1}]
T	temperature [K]
$U_{effective}$	U_t U_{gas} drop velocity [m s^{-1}]
U_{Nozzle}	liquid velocity into the nozzle [m s^{-1}]
VOC	volatile organic compound
$[VOC]_{equi}$	VOC concentration in equilibrium [ppm]
$[VOC]_{before\ equilibrium}$	VOC concentration before equilibrium [ppm]
V_{air}	volume of air in the balloon [L]
V_{liquid}	volume of vegetable oil added [L]
$V_{M\ air}$	molar volume of air [L/mol]
$V_{M\ liquid}$	molar volume of the vegetable oil [L/mol]
x	molar fraction of toluene in the liquid phase [dimensionless]
y	molar fraction of toluene in gas phase [dimensionless]
y_{in}	molar fraction of toluene within the gas phase (air) at the bottom of the column.
y_{out}	molar fraction of toluene at the top of the column.
Z	tower height [m]
Ω	effective cross section of the tower [m^2]
α	cover rate [dimensionless]
μ	viscosity [Pa s]
ρ	density [kg m^{-3}]
σ	surface tension [N m^{-1}]

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